

## DENDRITIC EMULSIFIERS AND METHODS FOR THEIR USE AND PREPARATION

### RELATED APPLICATIONS

This application is a National Stage application of International Application No. PCT/US2010/057049 filed Nov. 17, 2010, which claims the benefit of U.S. Provisional Application No. 61/261,963, filed Nov. 17, 2009, the entire contents of which are hereby incorporated herein by reference.

### TECHNICAL FIELD

The present teachings relate generally to the preparation and use of emulsifiers.

### BACKGROUND

Emulsifiers are used in the food industry (and non-food industries) to form oil-in-water emulsions for the dispersion of hydrophobic components, such as nutrients (e.g., omega-3 fatty acids), flavors, regular lipids, and the like. Emulsifiers govern emulsion stability—a key factor in food quality—thereby protecting against coalescence (e.g., aggregation and creaming) and oxidation (which leads to rancidity and hazardous compounds).

Among the different types of emulsifiers, biopolymer-based emulsifiers typically exhibit a stronger capacity for emulsion stabilization than small molecule-based surfactants, forming a thick interfacial layer that allows for more effective steric repelling among oil droplets. If the biopolymer is charged, static repelling is also stronger for biopolymer-based interfacial layers. In addition, the migrations of oxidative compounds (e.g., oxygen, metal ions, and radicals) are greatly reduced due to the thick layer.

Gum arabic and starch octenyl succinate (starch-OSA) are two biopolymer-based emulsifiers that have been used in prior efforts to increase emulsion stability.

### SUMMARY

The scope of the present invention is defined solely by the appended claims, and is not affected to any degree by the statements within this summary.

By way of introduction, a dendritic emulsifier for forming an oil-in-water emulsion includes an anhydride-modified phytoglycogen or glycogen-type material.

A method of preparing an oil-in-water emulsion includes (a) combining oil, water, and a dendritic emulsifier; and (b) mixing a combination of the oil, water, and dendritic emulsifier. The dendritic emulsifier includes an anhydride-modified phytoglycogen or glycogen-type material.

A method of preparing a dendritic emulsifier includes reacting an anhydride with a phytoglycogen or glycogen-type material in solution, thereby forming an anhydride-modified phytoglycogen or glycogen-type material. The anhydride is selected from the group consisting of succinic anhydride, octenyl succinic anhydride, and a combination thereof.

### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a transmission electron microscopy (TEM) image of a phytoglycogen (scale bar=100 nm).

FIG. 2 shows a representative chemical scheme for the reaction of phytoglycogen (PG-OH) with an anhydride reagent.

FIG. 3 shows an illustration of interfacial layers over oil droplets in various oil-in-water emulsions, wherein the layers are formed by small molecules (upper left), macromolecules (upper right), multilayer (bottom right), and dendritic molecules (bottom left).

FIGS. 4a and 4b show graphs of intensity vs. particle size distribution for oil-in-water emulsions at different stages.

### DETAILED DESCRIPTION

Modified phytoglycogen and glycogen-type materials with a strong capacity for stabilizing emulsions have been discovered and are described hereinbelow. The amphiphilic dendritic molecule phytoglycogen octenyl succinate (PG-OSA) has shown superior performance in forming and stabilizing oil-in-water emulsions. It was further discovered that PG-OSA has a much greater ability to stabilize emulsions than either starch octenyl succinate (starch-OSA) or gum arabic (GA). Moreover, in view of the abundant availability of phytoglycogen—which is a major carbohydrate in commercial sweet corn—PG-OSA has significant potential for industrial application. In addition, it is envisioned that large-scale production of glycogen can be readily achieved by industrial fermentation of yeast.

Throughout this description and in the appended claims, the following definitions are to be understood:

The term “dendritic” refers to a highly branched chemical structure.

The phrase “phytoglycogen or glycogen-type material” refers to dendritic (i.e., highly branched)  $\alpha$ -D-glucan and carbohydrate nanoparticles. The term “phytoglycogen” generally refers to material that is derived from plants while the term “glycogen” generally refers to material that is derived from microbes and/or animals.

By way of introduction, phytoglycogen is a water-soluble glycogen-like  $\alpha$ -D-glucan in plants. The largest source of phytoglycogen is the kernel of the maize mutant su1, a major genotype of sweet corn. The su1 mutation leads to a deficiency in SU1, an isoamylase-type starch debranching enzyme (DBE). In the biosynthesis of starch, starch synthase (SS), starch branching enzyme (SBE), and DBE work together to produce starch granules, with the primary role of DBE being to trim abnormal branches that inhibit the formation of starch crystals and granules. When there is a lack of DBE, the highly branched phytoglycogen is formed in the replacement of starch granules. FIG. 1 shows a TEM image of phytoglycogen nanoparticles with most particles ranging in size from 30 to 100 nm.

The highly branched structure of phytoglycogen results in its unusually high molecular density in dispersion. For example, in rice, the dispersed molecular density of phytoglycogen is over 10 times that of starch. Similarly, the molecular density of phytoglycogen from maize is around 1000 g/mol/nm<sup>3</sup> as compared to about 50 g/mol/nm<sup>3</sup> for amylopectin. The high density of phytoglycogen provides structural integrity and allows for dense grafting of functional groups.

Each phytoglycogen particle contains hundreds or thousands of glucan chains forming a highly packed structure. Without wishing to be bound by a particular theory or to in any way limit the scope of the appended claims or their equivalents, it is presently believed that that the spherical phytoglycogen particle grows from the non-reducing ends on the surface by periodic branching and elongation of chains. In phytoglycogen, there is no long chain that connects individual clusters as in the case of an amylopectin molecule, which suggests a fundamental structural difference between phytoglycogen and amylopectin.